Negative Ion Processes for the Unambiguous
Identification of Polycyclic Aromatics*

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The unambiguous identification of polycyclic aromatic hydrocarbons (PAH) in a complex mixture is a difficult analytical problem. Combined gas chromatography/ mass spectrometry is one of the most frequently used techniques for the analysis of PAH in complex mixtures due to its ability to separate components prior to detection by the mass spectrometer. Conventional electron impact ionization is often limited in its ability to identify PAH at the isomeric level because PAH generally yield strong molecular ions with little or no fragmentation which would allow isomeric species to be differentiated. The presence of a particular isomer in a mixture can have a profound effect on the mixture's biological activity. For example, benzo(a)pyrene is a well-known potent carcinogen, whereas its isomer, benzo(e)pyrene is relatively inactive. Therefore, it is important to be able to identify these compounds and even quantitatively determine their levels in the presence of each other in order to fully assess a mixture's potential risk with respect to human health.

A number of mass spectral techniques have been reported in recent years as a means of differentiating isomeric PAH, including mixed charge exchange chemical ionization (1,2), pulsed positive and negative chemical ionization using mixed reagents (3,4), and metastable ion spectra (5). These methods rely upon comparing the ratios of the observed ion intensities for the differentiation of the isomeric compounds. This would limit the usefulness of these techniques to compounds for which standards were available. Ideally, one would like an analytical technique which would not rely on the availability of authentic compounds. This is particularly true in the case of PAH and alkyl-substituted PAH, where thousands of isomers are possible, but relatively few are commercially available.

Recently, we have been investigating the use of electron capture negative ion processes for the differentiation of isomeric PAH (6). Most PAH have positive electron affinities ranging in magnitude from a few tenths to over one electron volt (7). Electron capture reactions of PAH using both electron capture chromatographic detectors (8,9) and negative ion chemical ionization mass spectrometry (6,10-12) have been reported. In this paper, negative ion processes have been investigated for the differentiation of isomeric PAH based upon relative differences in electron affinities. The use of these processes in both negative ion chemical ionization mass spectrometry and a newly developed chromatographic detector will be discussed.

In the electron capture negative ion chemical ionization (CI) experiments, methane was used as a buffer gas and introduced into the ion source of a Hewlett-Packard 5985B quadrupole mass spectrometer at a pressure of a few tenths of a torr (6). Electron bombardment was used to ionize the methane. Under these conditions, electrons with nearly thermal energy are produced and can be captured by compounds to form anions. Initial experiments using these conditions revealed that some PAH undergo electron capture to form molecular anions, M^-, whereas others did not ionize, as shown in Figure 1.

Further studies using over forty PAH suggested that the ionization behavior of the PAH under electron capture conditions was related to their electron affinities. Electron affinities (EA) of complex molecules are difficult to measure experimentally (7). However, EA values may be estimated from Hückel molecular orbital calculations (13). The EA of a PAH is linearly related to the energy of the lowest unoccupied molecular orbital, ϵ_{LUMO}, where

$$\epsilon_{LUMO} = \alpha + m_{m+1}\ \beta \qquad\qquad 1)$$

and α and β are defined as the Coulomb and resonance integrals, respectively, and m_{m+1} is the coefficient of energy for the LUMO. The values of m_{m+1} have been calculated for a large number of PAH and are available in a number of compilations (14-16). Because m_{m+1} is linearly related to ϵ_{LUMO}, which is in turn linearly related to the electron affinity of a molecule, m_{m+1} values may be used as a relative measure of EA values (6).

Using adiabatic EA values which had been calculated by Younkin et al., (17), as well as m_{m+1} values, it was found that the ionization behavior of the PAH fell into two groups with respect to their EA values, as shown in Table 1. Those with EA values greater than 0.5 eV (or m_{m+1} values greater than -0.42) ionized to produce molecular anions. Compounds with lower EA values did not ionize and thus were not observed. This difference in ionization behavior permits a number of isomeric PAH to be distinguished. For example, fluoranthene and pyrene, both with a molecular weight of 202, are readily distinguished under the negative ion CI conditions, with only fluoranthene yielding a molecular anion. Perhaps the most important differentiation, however, is between the two benzopyrene isomers. As stated previously, benzo(a)pyrene is a much more potent carcinogen than its isomer, benzo(e)pyrene. Under negative ion CI conditions, only benzo(a)pyrene is ionized, allowing it to be identified readily and quantitatively determined in the presence of its isomer without interference.

The addition of alkyl groups to a PAH is predicted to alter the α term in Equation 1 only slightly and thus have little effect on EA value of the alkylated PAH (13). This prediction has been confirmed in studies using alkyl-substituted PAH, which show that these compounds may be differentiated in a manner similar to their parent compounds. This eliminates the need for standard compounds to differentiate these compounds as well.

A number of nitrogen-substituted PAH have also been studied by the electron capture negative ion CI techniques, and the same type of isomeric differentiation is observed. A few of the compounds which have been studied are shown in Table 2. The addition of a nitrogen into the ring system of a PAH raises the electron affinity of the azaarene slightly above that of the parent PAH. This is observed clearly in the case of acridine, which yields molecular anions, in contrast to the corresponding PAH, anthracene, which does not ionize.

An example illustrating the use of electron capture negative ion CI is shown in Figure 2. In this figure are three total ion chromatograms of a PAH isolate from a coal-derived liquid. The lower trace was obtained by conventional electron impact ionization. The middle trace was obtained by methane chemical ionization in the positive ion mode. In both of these chromatograms, all of the compounds are ionized and the profiles appear essentially identical. The upper trace was obtained in the electron capture negtive ion CI mode using methane as the buffer gas. In this chromatogram, only compounds with EA values over 0.5 eV are observed, allowing a number of isomers to be distinguished. Most notable is the differentiation of fluoranthene (peak 1) and pyrene (peak 2), as well as the C_2-substituted fluoranthenes (peak 4) and the C_2-substituted pyrenes (peak 5). Another feature of this technique is also observed in Figure 2. Higher molecular weight compounds are often difficult to observe using chromatographic methods. This is due to the fact that the chromatographic efficiency drops off as the compounds are retained on the

column for longer periods of time. In the negative ion CI mode, however, these higher molecular weight PAH are more clearly observed than with either electron impact or positive ion chemical ionization. The higher sensitivity of the compounds in the electron capture process is due to the faster reaction rates of electron-molecule reactions, in general, and the higher capture cross-section and electron affinities of these larger PAH. The ability to detect these larger-ring PAH is especially important in the analysis of complex mixtures with respect to human health risks because these compounds generally have higher biological activity than compounds with fewer aromatic rings. Compounds with molecular weights in excess of 350 have been observed in coal-derived liquids using this technique.

Electron capture detectors (ECD), which are widely used in chromatography, employ chemical processes which are similar to those used in electron capture negative ion CI experiments. In the case of an ECD, the detector is operated at atmospheric pressure instead of a few tenths of a torr, and a source of β-radiation, usually ^{3}H or ^{63}Ni, is used instead of an electron filament for the ionization of the buffer gas. Typically, a mixture of 10% methane in argon is used as the buffer gas. The particles collide with the argon to produce metastable ions, which then ionize methane to produce thermal electrons. As a compound enters the detector cell and captures these electrons, the current measured at the anode decreases, producing the resulting signal.

Studies of PAH using an ECD have shown that some differentiation may be obtained based on the relative responses of the isomers (19). This differentiation can be enhanced with the addition of dopants to the buffer gas, such as oxygen and ethyl chloride (19,20). The similarity in the chemical processes used in an ECD and the negative ion CI experiments prompted the investigation of whether a chromatographic detector similar to an ECD but operated at lowered pressures would yield the same type of distinct responses for isomeric PAH as was observed in the mass spectrometry experiments.

A vacuum chamber was designed to contain a conventional ECD cell with a ^{63}Ni source. The chamber was constructed so that the pressure could be varied from a few tenths of torr to atmospheric. A separate line supplied the buffer gas to the cell and a fused silica capillary column was connected directly to the detector. A more detailed description of the detector design has been submitted for publication.

A mixture of four PAH, phenanthrene, anthracene, fluoranthene, and pyrene, were first studied with the detector at atmospheric pressure. As shown in Figure 3a, only three of the four compounds were detected with the detector operated in the conventional ECD mode. Phenanthrene has a low electron affinity (0.03 eV), and does not undergo electron capture (17,19). When the pressure in the detector was lowered to about one torr, the direction of the chromatographic peaks were reversed, as shown in Figure 3c. This reverse response indicates that the electron population in the cell increased as the compounds eluted, representing electron emission by the compounds themselves. The emission process yields approximately equal response for all four compounds, in contrast with the distinctly different relative responses observed in the electron capture mode at atmospheric pressure.

When the pressure within the variable pressure detector was increased to approximately 200 torr, a third type of response was observed, as shown in Figure 3b. The peaks for the two isomers fluoranthene and pyrene are in the electron capture and electron emission modes, respectively, allowing them to be readily distinguished. The peak for phenanthrene is in the electron emission mode and that for anthracene is at a cross-over point between emission and capture modes. At lower pressures, the peak would be negative, indicative of electron emission, and at higher pressures, the peak would be positive, indicative of electron capture. This demonstrated that differentiation of various isomers can be

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obtained with this new detector by selecting pressures where one isomer would be in the electron capture mode, while the other isomer would be in the electron emission mode. An example of this is shown in Figure 4. In the top profile, the detector was operated in the emission mode and all components of a mixture of alkyl-substituted phenanthrenes and anthracenes are observed. Raising the pressure to 175 torr causes the substituted anthracenes to cross-over to the electron capture mode, allowing them to be clearly differentiated from the isomeric alkyl-substituted phenanthrenes.

This variable mode ionization detector can be operated in three distinct modes just be changing the pressure within the cell. At atmospheric pressure, it can be operated as a conventional ECD. At low pressures, it can be operated in the electron emission mode and very level responses for each compound can be obtained, not unlike electron impact ionization or flame ionization response. Finally, at intermediate pressures, a high degree of selectivity for various compounds may be obtained. In this latter mode, the same type of isomeric differentiation observed in the negative ion CI mass spectrometry experiments can be obtained, but without the need for the mass spectrometer. Not only can the detector be used in this mode to distinguish various isomers, but also to selectively detect one class of compounds in the presence of other classes.

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Table 1. Electron capture CI response of PAH

Compound	Molecular weight	$-m_{m+1}$[a]	EA[b]	Base peak m/z
Acenaphthylene	152	0.285	0.77	152
Anthanthrene	276	0.291	-[c]	276
Indeno(1,2,3-cd)pyrene	276	0.293	-	276
Benzo(i)fluoranthene	252	0.312	-	252
Benzo(a)pyrene	252	0.371	0.64	252
Fluoranthene	202	0.371	0.63	202
Benzo(b)fluoranthene	252	0.377	-	252
Benzo(ghi)fluoranthene	226	0.378	-	226
Azulene	128	0.400	0.77	128
Benzo(k)fluoranthene	252	0.401	-	252
Anthracene	178	0.414	0.49	-[c]
Dibenzo(a,i)pyrene	302	0.522	-	302
Dibenzo(a,e)pyrene	302	0.422	-	302
Benzo(ghi)perylene	276	0.439	0.51	276
Pyrene	202	0.445	0.45	-
Benzo(a)anthracene	228	0.452	0.42	-
Dibenzo(a,i)anthracene	278	0.492	0.33	-
Benzo(e)pyrene	252	0.497	0.35	-
1,2,3,4-Dibenzanthracene	278	0.499	0.34	-
Picene	278	0.502	0.29	-
Chrysene	228	0.520	0.26	-
1-Phenylnaphthalene	204	0.522	-	-
Coronene	300	0.539	0.32	-
Benzo(c)phenanthrene	228	0.568	0.18	-
2-Phenylnaphthalene	204	0.565	-	-
p-Terphenyl	230	0.593	-	-
Phenanthrene	178	0.605	0.03	-
Naphthalene	128	0.618	-0.06	-
Biphenyl	154	0.705	-	-

[a]Calculated coefficient of energy for LUMO from Refs. 14, 15, and 16.
[b]Calculated electron affinity values from Ref. 17.
[c]The - signifies that no response was observed.

Table 2. Negative ion CI response of selected azaarenes

	MW	Negative Ion CI Response
Acridine (9-azaanthracene)	179	179
Phenanthridene (9-azaphenanthrene)	179	-
2-azafluoranthene	203	203
1-azapyrene	203	203
1-azachrysene	229	-
10-azabenzo(a)pyrene	253	253

Fig. 2. Total ion chromatograms of PAH isolate from a coal-derived liquid obtained with conventional electron impaction ionization (bottom), positive ion methane CI (middle), and negative ion CI (top).
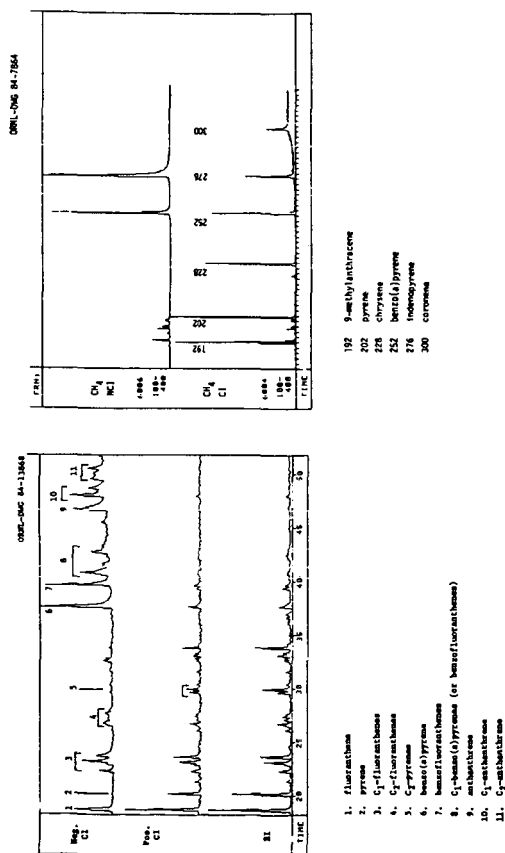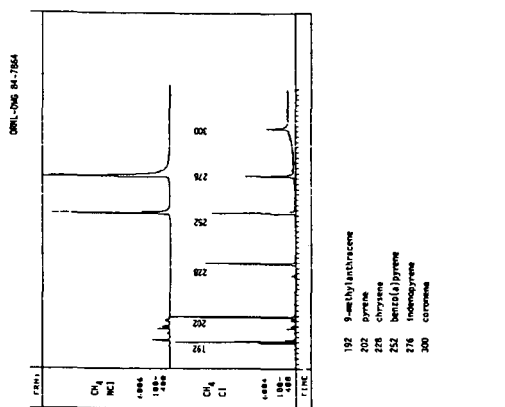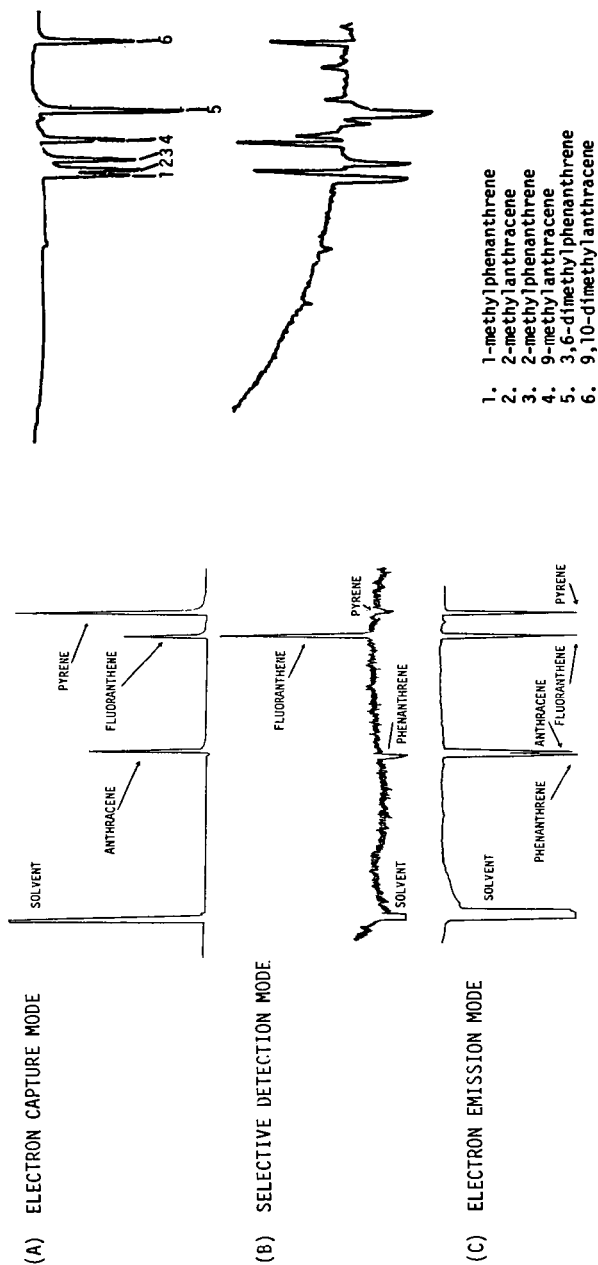

Fig. 1. Total ion chromatograms of six component PAH standard in methane positive ion CI mode (bottom) and negative ion CI mode (top).

1. 1-methylphenanthrene
2. 2-methylanthracene
3. 2-methylphenanthrene
4. 9-methylanthracene
5. 3,6-dimethylphenanthrene
6. 9,10-dimethylanthracene

Fig. 4. Variable pressure ionization detector response at low pressures (emission mode, top), and at intermediate pressures (selective mode, bottom).

(A) ELECTRON CAPTURE MODE

(B) SELECTIVE DETECTION MODE

(C) ELECTRON EMISSION MODE

Fig. 3. Different modes of operation of variable pressure detector at atmospheric pressure (A), 200 torr (B), and 1 torr (C).

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